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Short Report

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Theoretical studies of the suitability of imidazoly-pyridine as bidentate ligands for copper redox couples in the Dye Sensitized Solar Cell (DSSC) application

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Abstract

Copper complex redox couples have emerged as alternative redox mediator to iodide/triiodide redox couple for DSSC devices. The copper redox couples enable high and tunable voltage in DSSC devices. However, the Cu(II) species in a typical copper redox couples are strongly electrophilic towards injected electrons in TiO₂ thereby promoting recombination and decreases the cell performance. Although 4-tertbutylpyridine (TBP) passivation of TiO₂ surface reduces the extent of the recombination, its interaction with Cu(I) complex in a copper redox couples may be detrimental to the cell performance. Therefore, rational selection of ligands of the copper complexes is critical in obtaining high voltage and performance. In this work, Density Functional Theory (DFT) was adopted to screen four imidazoly-pyridine bidentate ligands: 2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine (MDIP); 2-(1-methyl-1H-imidazol-2-yl)pyridine (MIP); 2-(1,4,5-trimethyl-1H-imidazol-2-yl)pyridine (TMIP) and 1-methyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (MPBI). Calculated binding constants of interaction of 4-tertbutylpyridine (TBP) with the imidazoly-pyridine copper complexes indicated Cu(I) complexes of MDIP and MIP interact strongly with TBP. This has adverse effects on device voltage, thus, making MDIP and MIP ligand unsuitable. But Cu(I) complexes of TMIP and MPBI interact very weakly with TBP, indicating they are suitable ligands for copper complex redox couples for DSSC application.

Key words: DFT, copper complexes, redox mediator, ligands, DSSC

1 Introduction

The introduction of outer-sphere one electron exchange transition metal complex species as redox mediator is a turning point in the development of dye sensitized solar cell (DSSC). Iodide/triiodide (I⁻/I₃⁻) redox couple electrolyte was the dominant redox mediator used in the fabrication of DSSC device for about two and half decades (Pawlus and Jarosz, 2022; Saygili et al. 2019). In addition to I⁻/I₃⁻ couple, Lewis base additive such 4-tertbutylpyridine (TBP) is usually a constituent of the

electrolyte to improve the performance of the device. The I^-/I_3^- couple dominates the redox mediator role because of the very slow recombination kinetics between injected electrons in TiO_2 and the oxidized species of the I^-/I_3^- couple (I_3^-). However, the I^-/I_3^- redox couple suffers from high dye regeneration over potential which in turn translates into voltage loss in the resulting device. This problem is traced to the high activation energy and complicated two electron redox kinetics among the iodide species. However, transition metal complex species have simple kinetics and lower activation energy outer-sphere one electron exchange processes (Bignozzia et al. 2013).

Transition metal complex based redox mediators have enabled high voltage DSSC device than obtainable using I^-/I_3^- based ones. Moreover, there is flexibility of marching the frontier energy levels of the dye with those of the transition metal complex redox couple in order to maximize the DSSC voltage (Pawlus and Jarosz, 2022). Although cobalt, iron and copper-based complex redox mediators have enabled DSSC device with voltage > 1 , copper complex in particular, has attracted increased attention in recent times. A recent report showed that with the same ligand copper complex outperformed cobalt based one as redox mediator in a DSSC device (Selvaraj et al. 2021). This was attributed to the lower coordination number of copper ions resulting in lower molecular mass of copper complexes compared to cobalt and iron counterparts. Thus, the lighter copper complexes diffuse faster than the heavier cobalt and iron complexes (Srivishnu et al. 2021). Moreover, when the solvent dried out copper complex had been found to display hole transport via hopping mechanism, which is advantageous for fabrication of solid state DSSC device (Cao et al. 2017; Freitag et al. 2015).

Experimental and theoretical results had shown that TBP adsorption on TiO_2 results in the shift of the Fermi level TiO_2 upwards by transfer of vacancy excess charge into the unoccupied π orbital of TBP (Göthelid et al. 2011). This explains the higher open circuit voltage (V_{oc}) usually obtained with iodide based redox mediator electrolytes containing 4-TBP additive (Yang et al. 2018; Thu et al. 2020) [9-10]. The TBP had been shown to adsorb on unsaturated TiO_2 sites. Also the adsorbed TBP suppresses recombination between injected electron into TiO_2 and iodine and triiodide ion (Dürr et al. 2006; Xiong et al. 2008; Boschloo and Hagfeldt 2009). Thus, TBP becomes a standard additive in iodide/triiodide redox electrolytes. This legacy was carried over to copper complex redox electrolyte preparations.

However, in addition to the highlighted benefits, TBP interaction with $Cu(II)$ species in an electrolyte can alter the redox potential of the electrolyte. For instance, it has been shown that TBP reacts with bis(2,9-dimethyl-1,10-phenanthroline)copper(II), $[Cu(dmp)_2]^{2+}$, and leads to three new TBP-coordinated $[Cu(dmp)_2]^{2+}$ redox couples (Kannankutty et al. 2020). The new redox couples had more negative redox potential relative to pristine $[Cu(dmp)_2]^{2+}$, and had been linked to degradation of the cell performance. On the other hand, TBP coordinated $[Cu(dmp)_2]$ is also shown to suppress recombination losses thereby improving the cell performance (Fürer et al. 2020). Overall, the TBP additive complicates the cell operation. Therefore, it is desirable to replace TBP with non-copperphilic additive or use $[Cu(\text{ligand})_2]^{2+}$ species that are resilient to TBP-coordination. Thus, in this paper, we use DFT to study the binding characteristics of four bidentate imidazoly-pyridine ligands. We calculate the stability constant of $[Cu(\text{ligand})_2]^{+2+}$ and TBP- $[Cu(\text{ligand})_2]^{+2+}$ species to evaluate their resistance to TBP coordination.

2 Materials and Methods

2.1 Ligands

The four imidazole-pyridine ligands that were explored in this study are shown in table 1.

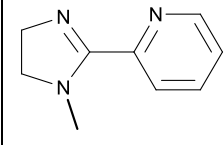
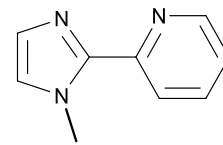
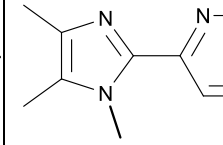
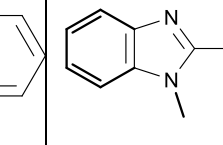
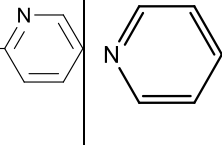
				
2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine	2-(1-methyl-1H-imidazol-2-yl)pyridine	2-(1,4,5-trimethyl-1H-imidazol-2-yl)pyridine	1-methyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole	4-tertbutylpyridine
MDIP	MIP	TMIP	MPBI	TBP

Table 1: Bidentate imidazole-pyridine ligands and 4-tertbutylpyridine

2.2 Computational Methods

All computations were performed using the Orca 4.2.1 quantum chemistry package (Neese et al. 2020). The choice of functional basis set was guided by the report of Schmidt et al.(2014). The geometries of the ligands and the complexes were optimized, using BP86 functional and def2-SVP def2/J D3BJ basis set for all atoms in the ligand and ma-def2-TZVPP for Cu. The frequency calculations were performed, using the same functional and basis set, but the optical properties were computed, using B3LYP functional. Calculations in solution were performed using the SMD solvation model. The model uses the CPCM algorithm with different radii to create the cavity and calculates a different non-electrostatic contribution, the cavity-dispersion-solvent structure, CDS term. Calculations were in gas phase unless specified otherwise. No symmetry limitations were imposed during the calculations. Quantum mechanical descriptors for characterizing the sigma donor (σ) and pie acceptance (π) acceptance for the ligands were calculated according to equations used by Raashid et al.(2013). The equations are defined as follows:

- According to Koopmans' approximation, $I \approx -E_{HOMO}$, $A \approx -E_{LUMO}$ (1)

Where I - Ionization energy, A - Electron affinity

- Chemical potential $\chi = -\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \approx -\frac{I + A}{2}$ (2)

- Hardness $\eta = \frac{1}{2} \left(\frac{\partial E}{\partial N} \right)_{v(r)} \approx \frac{I - A}{2}$ (3)

- Softness $S = \frac{1}{2\eta}$ (4)

- Electrophilicity index (ω) as a measure of the decrease in energy due to the maximal transfer of electrons from donor to an acceptor molecule

$$\omega = \frac{(-\chi)^2}{2\eta} \text{(5)}$$

- Reactivity indices, electrophilicity (ΔE_e) and nucleophilicity (ΔE_n) are defined as

$$\Delta E_e = \frac{(\mu - \eta)^2}{2\eta} \dots\dots\dots (6)$$

$$\Delta E_n = \frac{(\mu + \eta)^2}{2\eta} \dots\dots\dots (7)$$

3 Results and discussion

The optimized structures of the four imidazoly-pyridine based bidentate ligands and 4-terbutylpyridine are shown in Figure 1. The ligands have pyridine nitrogen and imine nitrogen as binding atoms and have N=C-C=N dihedral angles that are similar to those of 2,2'-bipyridine and phenanthroline ligands. Quantum chemical descriptors of the ligands calculated from optimized geometries, using equations (1)–(7), were tabulated in Table 2. Since the pyridine fragment in the imidazoly-pyridine ligands is identical, variation of the quantum chemical descriptors can be attributed to the imidazoly fragments. The LUMO energy levels of the ligands deepen with increase in aromaticity and rise with number alkyl substitution. Similar trend was displayed for HOMO, ionization energy, electron affinity and chemical potential. The hardness and softness values of MDIP, the ligand with imidazolidine fragment, is markedly different from those of MIP, TMIP and MPBI (ligands with imidazole fragment). Electrophilicity index and reactivity (especially nucleophilicity) of the found ligands were found to follow the same trend. These descriptors are related to HOMO-LUMO gap. TBP has wider HOMO-LUMO gap and its higher LUMO level culminates in stronger nucleophilicity than the four imidazoly-pyridine ligands.

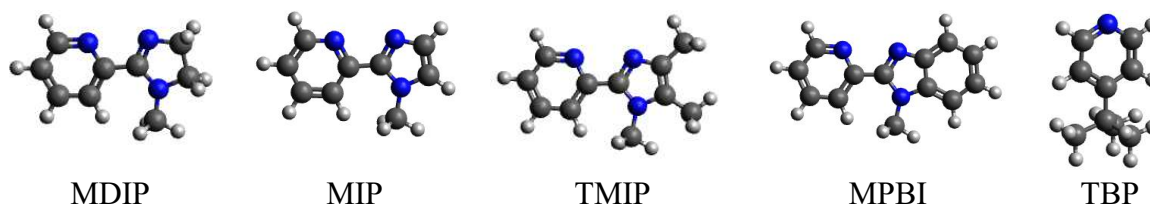


Figure 1: Optimized structures of the four imidazole-pyridine based bidentate ligands and 4-terbutylpyridine

Ligand	E_{LUMO}	E_{HOMO}	I	A	χ	η	S	ω	ΔE_e	ΔE_n
MDIP	-2.071	-4.529	2.071	4.529	-3.300	-1.229	-0.407	-4.430	-8.345	-1.744
MIP	-2.005	-5.277	2.005	5.277	-3.641	-1.636	-0.306	-4.052	-8.511	-1.228
TMIP	-1.869	-4.869	1.869	4.869	-3.369	-1.500	-0.333	-3.783	-7.902	-1.164
MPBI	-2.395	-5.408	2.395	5.408	-3.902	-1.507	-0.332	-5.052	-9.707	-1.904
TBP	-1.603	-5.660	1.603	5.660	-3.632	-2.029	-0.246	-3.250	-7.896	-0.633

Table 2: Calculated values of various quantum mechanical descriptors for four imidazole pyridine based bidentate ligands and 4-terbutylpyridine (in gas phase)

Because reported copper complex electrolytes used for DSSC are prepared with acetonitrile as solvent, we re-compute the optimized structures of the ligands in acetonitrile. As shown in Table 3, the recalculated descriptors followed the same trends as in the gas phase albeit with reduced values which account for solvation effect of solvent on the ligands. Subsequent computations on the ligands were carried out in acetonitrile medium.

Ligand	E _{LUMO}	E _{HOMO}	I	A	χ	η	S	ω	ΔE_c	ΔE_n
MDIP	-2.008	-4.831	2.008	4.831	-3.420	-1.412	-0.354	-4.142	-8.267	-1.428
MIP	-2.026	-5.398	2.026	5.398	-3.712	-1.686	-0.297	-4.086	-8.641	-1.212
TMIP	-1.985	-4.945	1.985	4.945	-3.465	-1.480	-0.337	-4.056	-8.261	-1.331
MPBI	-2.322	-5.585	2.322	5.585	-3.954	-1.632	-0.306	-4.790	-9.559	-1.652
TBP	-1.627	-5.867	1.627	5.867	-3.747	-2.120	-0.236	-3.311	-8.118	-0.624

Table 3: Calculated values of various quantum mechanical descriptors for four imidazole pyridine based bidentate ligands and 4-terbutylpyridine (in acetonitrile)

TBP is a popular additive in DSSC redox electrolyte including copper complexes redox couples. As indicated in the table 1, TBP is more nucleophilic than the four imidazolyl-pyridine ligands. One of the undesired effects of TBP in the DSSC redox electrolyte is interaction with the copper complexes redox couples. The interactions produce species with more negative redox potentials, thereby compromising the power conversion efficiency (PCE) of the DSSC device. In order to track the impact of the interactions on the redox potentials of the complexes, we correlated experimentally reported redox potentials of copper bipyridyl complexes (Von and Conradie 2011; Saygili et al. 2016) with their calculated orbital energies (Figure 2). A fair correlation coefficient was obtained between optimized ground state LUMO energies of the copper(I) complexes and experimentally reported redox potential of copper bipyridyl complexes. But a better correlation coefficient was obtained, using the excited state LUMO energies. Thus, the excited state LUMO energies were adopted for the estimation of the redox potentials of the imidazolyl-pyridine copper complexes. The redox potentials were estimated using the linear relation in Figure 2a and results were presented in Table 4.

In the absence of TBP coordination, the redox potentials of the Cu(I) complexes containing MDIP and MPBI are about the same and are more positive than those of MIP and TMIP. However, with TBP binding to the complexes, the redox potentials of MDIP and MIP are strongly lowered, while that of TMIP and MBPI are lowered by small margin. This shows that the TMIP and MBPI are resilient to TBP coordination. Similar trend was obtained for the Cu(II) complexes.

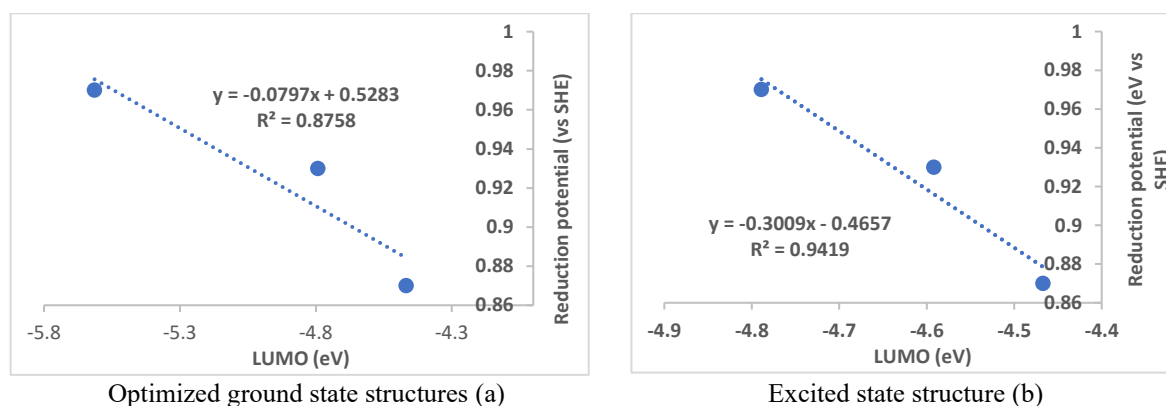


Figure 2: Computed LUMO vs Redox potentials (V vs SHE) of reported copper(I) complexes

Ligands	Redox Potentials Cu-imidazolyl-pyridines			
	$[\text{Cu}(\text{ligand})_2]^+$		$[\text{Cu}(\text{ligand})_2]^{2+}$	
	without TBP	with TBP	without TBP	with TBP
MDIP	0.95	0.82	2.06	1.86
MIP	0.88	0.79	2.06	1.74
TMIP	0.82	0.80	1.96	1.74
MPBI	0.94	0.91	2.02	1.87

Table 4: Extrapolated redox potentials of $[\text{Cu}(\text{ligand})_2]^{+/2+}$

The Frontier orbital energies of optimized structures of the copper complex were computed in gas phase and in acetonitrile and the results are shown in the table 5. The orbital energies show that coordination of the TBP lowers the LUMO and HOMO levels of the complexes. In acetonitrile, solvation of the complexes modulates their orbital energies and MPBI containing complexes have the deepest LUMO and HOMO levels. This suggests that Cu-MPBI based redox couple leads to higher cell voltage compared to those of Cu-MDIP, Cu-MIP and Cu-TMIP.

Ligands	In gas phase				In acetonitrile			
	$[\text{Cu}(\text{ligand})_2]^{2+}$		$[\text{Cu}(\text{ligand})_2\text{TBP}]^{2+}$		$[\text{Cu}(\text{ligand})_2]^{2+}$		$[\text{Cu}(\text{ligand})_2\text{TBP}]^{2+}$	
	ELUMO	EHOMO	ELUMO	EHOMO	ELUMO	EHOMO	ELUMO	EHOMO
MDIP	-9.176	-11.396	-8.516	-10.584	-3.422	-5.540	-3.259	-5.094
MIP	-9.179	-11.981	-8.404	-10.859	-3.409	-6.094	-3.128	-5.589
TMIP	-8.804	-11.296	-8.078	-10.608	-3.324	-5.853	-3.033	-5.550
MPBI	-9.005	-11.433	-8.515	-10.841	-3.602	-6.161	-3.404	-5.699

Table 5: HOMO and LUMO of $[\text{Cu}(\text{ligand})_2]^{+/2+}$ in gas phase and in acetonitrile

To further explore the resilience of the ligands to TBP coordination to Cu-ligand complexes, the binding constants of TBP coordination to the Cu complexes were calculated. The binding constant is a measure of resilience of Cu complexes to TBP coordination. Thus, it is considered a screening criterion for determining suitability of ligands in Cu-complex redox couples that are compatible with TBP for DSSC electrolyte preparation. The binding constants were obtained using equation 8 from the change in free energies of coordination of TBP to the $[\text{Cu}(\text{ligand})_2]^{+/2+}$ complexes (equation 9), which in turn were obtained using equation from the free energies extracted from frequency calculations of the reaction species.

$$\log K = - \frac{\Delta G_{[\text{Cu}-(\text{ligand})_2(\text{TBP})]^{n+}}}{2.303RT} \dots\dots\dots(8)$$

$$\Delta G_{[\text{Cu}-(\text{ligand})_2(\text{TBP})]^{n+}} = G_{[\text{Cu}-(\text{ligand})_2(\text{TBP})]^{n+}} - (G_{[\text{Cu}-(\text{ligand})_2]^{n+}} + G_{\text{TBP}}) \dots\dots(9)$$

As shown in Table 6, TBP binds strongly with all the Cu(II) complexes. This had been shown to be beneficial to DSSC performance because the TBP coordination modulates the orbital energies of the resulting Cu(II) species, thereby reducing the tendency of undesired recombination of injected electron into TiO_2 with the electrophilic $[\text{Cu}(\text{ligand})_2]^{2+}$ complexes (Fürer et al. 2020). Table 6 also indicated that TBP binds strongly to $[\text{Cu}(\text{MDIP})_2]^+$ and $[\text{Cu}(\text{MIP})_2]^+$, but

$[\text{Cu}(\text{TMIP})_2]^+$ and $[\text{Cu}(\text{MPBI})_2]^+$ are resistive to TBP coordination. While TBP coordination to $[\text{Cu}(\text{ligand})_2]^{2+}$ complexes is desirable toward improved DSSC cell performance, its coordination to $[\text{Cu}(\text{ligand})_2]^+$ complexes lowers the obtainable cell voltage. Hence, the low binding constants of TBP coordination to $[\text{Cu}(\text{TMIP})_2]^+$ and $[\text{Cu}(\text{MPBI})_2]^+$ is advantageous for their suitability as redox mediator for DSSC applications.

Ligands	Cu(I)		Cu(II)	
	$\log K$	K	$\log K$	K
MDIP	30.47	2.934×10^{30}	7.315	2.064×10^7
MIP	1.340	21.91	14.17	1.480×10^{14}
TMIP	-21.64	2.313×10^{-22}	10.82	6.575×10^{10}
MPBI	-23.58	2.610×10^{-24}	7.593	3.918×10^7

Table 6: Binding constant of coordination of TBP to $[\text{Cu}(\text{ligand})_2]^{+/2+}$ in acetonitrile

4 Conclusion

Copper complex redox mediators is bringing about renaissance in dye sensitized solar cell fabrication. Although, copper complex redox mediators afford high cell voltage, the Cu(II) species in the redox couples are strongly electrophilic towards injected electrons in TiO_2 , thereby driving undesired recombination that decreases the cell performance. 4-tertbutylpyridine (TBP) is a common additive in copper complex redox mediator preparation to passivates the TiO_2 surface and reduce the extent of the recombination. However, TBP can also interact with the redox couple species. While TBP interaction with Cu(II) species in a redox couple is advantageous, its interaction with Cu(I) species is detrimental to cell performance. Copper redox couples that will meet this requirement will entails rational ligand selection for the copper complex. In this study, we use DFT to screen four imidazoly-pyridine bidentate ligands: MDIP, MIP, TMIP and MPBI. Calculated binding constants of interaction of TBP with the imidazoly-pyridine copper complexes indicated Cu(I) complexes of MDIP and MIP interact strongly with TBP, making them fall short of set criterion. But Cu(I) complexes of TMIP and MPBI interact very weakly with TBP, fulfilling the set criterion and their suitability as ligands in copper complex redox couples for DSSC application.

Conflict of Interest

Not applicable

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Declarations

Ethical Approval

Not applicable

Consent to participate

Not applicable

Consent to publish

Not applicable

Informed Consent

Not applicable

Data availability statements

The input files for orca calculations were set at large print. The output files generated are large but they are available from the corresponding author on reasonable request.

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